Concepts of Chemistry for Engineering
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Lecture 56
Acid-base and Solubility Equilibria

Welcome to this next segment of thermodynamic discussion and its applications. So, far in the previous section we have discussed the application of thermodynamics in the form of electrochemical cells and find out the Nernst equation and how we can use the Gibbs free energy to connect it to the electrochemical potential of a system and find out what is the overall change in the electrochemical potential with respect to the equilibrium of the system. Now, in this particular section, we will look into acid base equilibria and solubility equilibria. So, let us get started.

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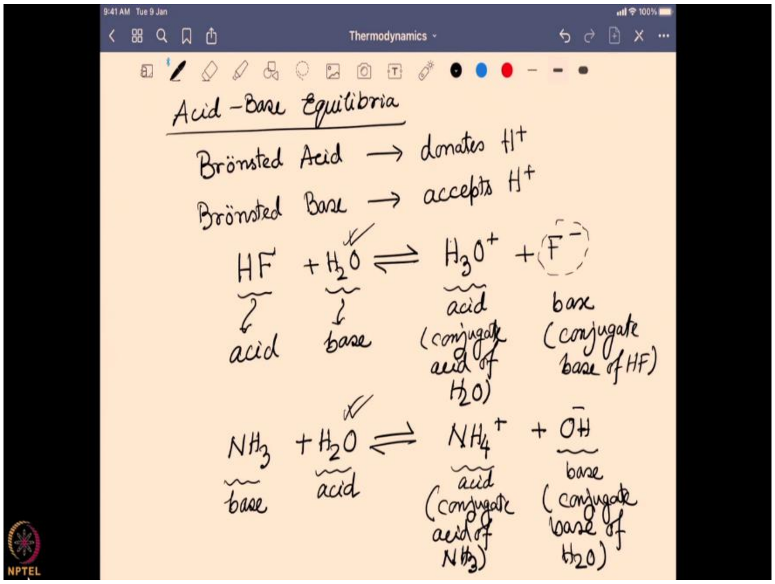

Acid-Base Equilibria

Brönsted Acid → donates H^+

Brönsted Base → accepts H^+

$$\underbrace{HF}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons \underbrace{H_3O^+}_{\text{acid (conjugate acid of } H_2O)} + \underbrace{F^-}_{\text{base (conjugate base of HF)}}$$

$$\underbrace{NH_3}_{\text{base}} + \underbrace{H_2O}_{\text{acid}} \rightleftharpoons \underbrace{NH_4^+}_{\text{acid (conjugate acid of } NH_3)} + \underbrace{\bar{O}H}_{\text{base (conjugate base of } H_2O)}$$

So, in this section we will mostly look into acid-base equilibria. So, what is an acid and what is in base? So, if we look into the definition given by Bronsted Acid, it is nothing but a system that can donate a proton (H^+), and what is a Bronsted base? Bronsted base is a system which actually accepts the proton and binds to it.

So, acid is which actually leaves a proton, base which actually binds a proton. So, to give you an example, let us take an example of HF hydrofluoric acid, if we put that in water, what happens? It actually goes into an equilibrium where it leaves a proton and this proton binds with the water to produce protonated water or H_3O^+ the hydronium ion and a fluoride ion F^-.

Over here HF is actually leaving the proton, so this is an acid and water is accepting the proton, so this is actually nothing but a base. Now, when HF the acid gives the proton, it also creates a base over here and that is known as the conjugate base of HF. So, conjugate base is nothing but you start with an acid and relieve the proton whatever is remaining it is going to be the conjugate base.

On the other hand, this base when it abstracts a proton, it creates this system H_3O^+ which is an acid because it can give the proton and go back to the original state H_2O , so this(HF) is known as acid and this (H_3O^+) is also known as the conjugate acid of H_2O where H_2O is acting as a base over here. So, this is all the equilibrium is happening over here.

Similarly, if we consider a base like ammonia and put that in water, then what happens? Now, over here, ammonia itself is going to abstract a proton from water and creates this ammonium ion and leaves hydroxide ion. Now over here, you can see out of ammonia and water, it is water which is actually giving the proton out, so this is the acid.

And ammonia is abstracting the proton, so it is acting as a base, out of this ammonium and hydroxide ion, ammonium is the system which can give a proton out so that is the acid and it is known as the conjugate acid of the base we discussed about ammonia. So, conjugate acid is nothing but the protonated version of the base. Whereas, hydroxide ion is a base because it can abstract a proton and go back to the water form, so this is known as the conjugate base of the acid and over here the acid is water.

So, you can see over here the water in one place is acting the role of an base and in one place it is acting the role of an acid. So, it can show both the version of acid and base activities, so it is known as amphi-directional directional character, it can be both acid it can be both base. At the same time, it is abstracting a proton and creating H_3O^+ it is acting as a base when it is leaving a proton and forming hydroxide it is acting as acid. So, now one very important thing is that how do we know where do I stand with respect to this equilibrium?

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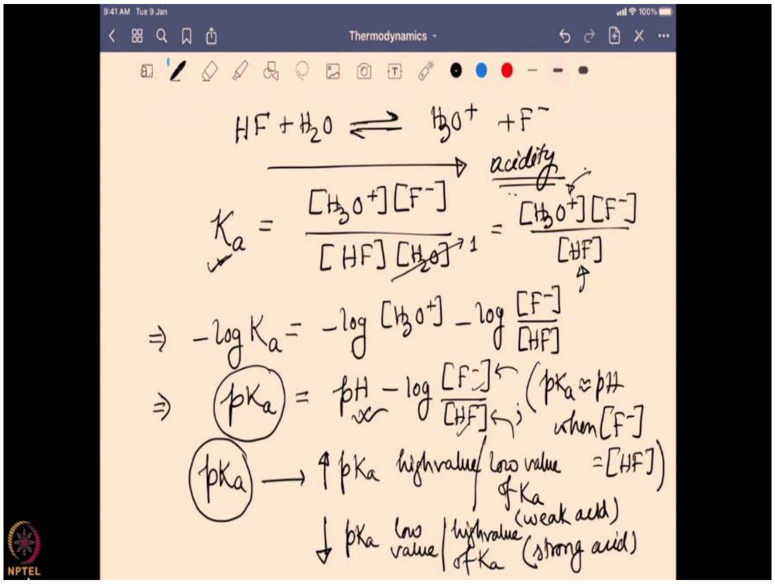

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

$\longrightarrow$ acidity

$$K_a = \frac{[H_3O^+][F^-]}{[HF]\cancel{[H_2O]}^{\to 1}} = \frac{[H_3O^+][F^-]}{[HF]}$$

$$\Rightarrow -\log K_a = -\log[H_3O^+] - \log\frac{[F^-]}{[HF]}$$

$$\Rightarrow \boxed{pK_a} = pH - \log\frac{[F^-]}{[HF]}; \left(pK_a \approx pH \text{ when } [F^-] = [HF]\right)$$

$\boxed{pKa} \longrightarrow$ ↑ pKa high value / low value of Ka (weak acid)

↓ pKa low value / high value of Ka (strong acid)

So, now just say I have in general hydrofluoric acid again, it is in presence of water creating the hydronium ion plus fluoride ion, now where it is standing so more the reaction goes to the forward direction it is going to create more protons in the hydrated form and that means it is going to show more acidity, because basically acidic means more protons availability, and more is the dissociation of the reaction in the forward direction more acidic it will be.

So, the acidic strength of a system we can measure from this equilibrium constant value (K_a) for this reaction in the forward state and we can write it as $\frac{[H_3O^+][F^-]}{[HF][H_2O]}$. Now, the concentration of H_2O is generally too much, so there is very little change in the concentration of water during the reaction, so we can actually take the activity of water is actually close to 1 in this case, so we can ignore that and we can just say the Ka value depends on $\frac{[H_3O^+][F^-]}{[HF]}$.And it is quite straightforward you can see the lower amount of HF present and higher amount of H_3O^+present higher will be the K_a value and that means stronger will be the acid and it is quite obvious from there because it means the HF is getting dissociated more so, less and less amount of HF is present in the solution. And more is the dissociation of the HF more will be the concentration of the H_3O^+.

Now, this equation we can actually modify a little bit by putting -log on both sides and we get the following -log of H_3O^+ and I am just taking rid of the other part $[F^-]/[HF]$ that means by equilibrium between HF and fluoride and over there this -log Ka is defined as pKa whereas -log of H_3O^+ is nothing but pH of the solution especially in water - log of $[F^-]/[HF]$. $pK_a = pH - \log\frac{[F^-]}{[HF]}$

And now you can see it the pKa value can be measured with respect to the pH of the solution and with respect to the amount of fluoride ion and HF acid present in the solution, and with respect to that I can measure the pH and when they will be equilibrated both of them are same at that time pKa will be equal to pH, when F minus concentration will be equal to HF and that is exactly the system we actually use for a titration experiment a pH titration experiment and find out where the pKa becomes equal to the pH and from there we can have a clear idea of what is the pKa of an acid.

As it is a -log value of Ka high value of pKa means a low value of Ka that means a low dissociation a weak acid. Whereas, a low value of pKa means high value of Ka that means it is a huge dissociation happening that means it is a strong acid. So, from here we can easily define the acid strength of a system.

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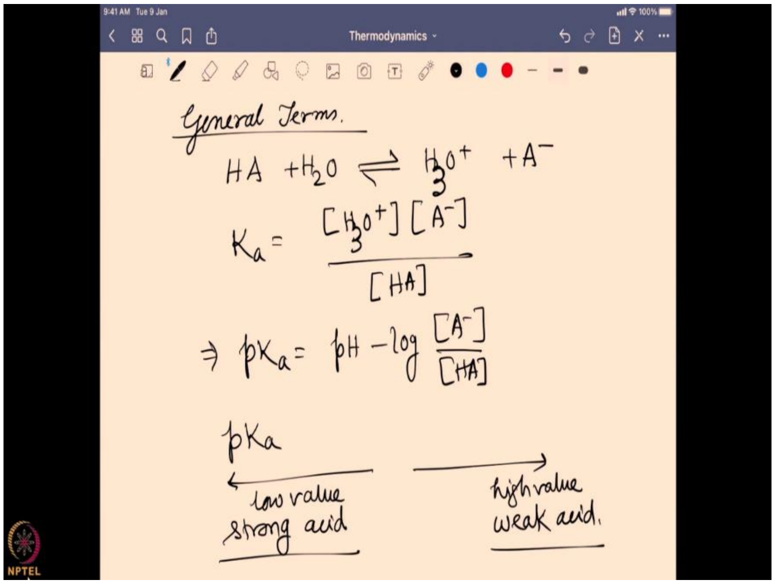

General Terms.

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$K_a = \frac{[H_3O^+][A^-]}{[HA]}$

$\Rightarrow pK_a = pH - \log\frac{[A^-]}{[HA]}$

pKa

← low value strong acid

→ high value weak acid.

And if we want to write it more generally we can imagine an acid HA which is in presence of water is giving me $H_3O^+ + A^-$ and that Ka value can be given as $\frac{[H_3O^+][A^-]}{[HA]}$ again we are not considering the water because it is highly concentrated or it is present in high concentration compared to the other acids and over there we can define pKa value which is nothing but $pK_a = pH$

– log$\frac{[A^-]}{[HA]}$ and from there we can define the pKa value low value and pKa value can also go to the high value, a low value of pKa means it is actually a strong acid, whereas a high value of pKa means it is weak acid.

So, this is what we can define from an acid base equilibrium from these equations and again over here the equilibrium constant and its connection to this thermodynamic terms give us an idea what is actually happening and now we can know that pKa value is nothing but a definition of the equilibrium constant value.

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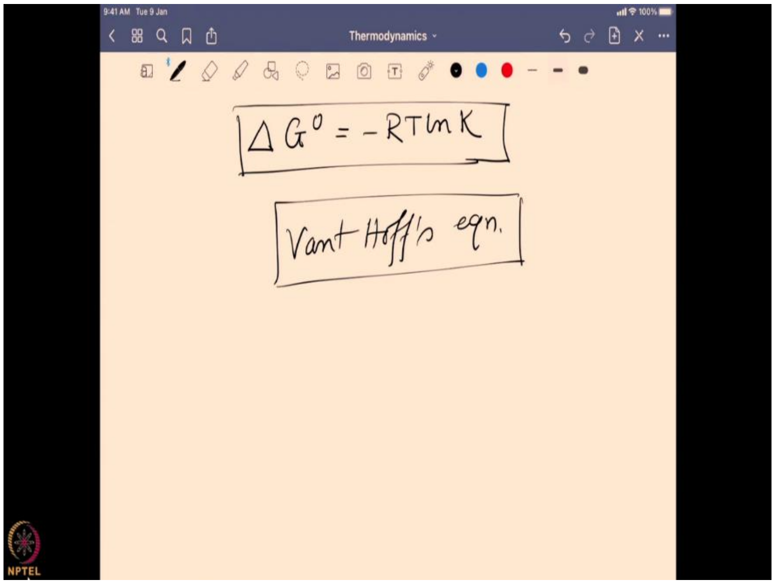

$$\boxed{\Delta G^0 = -RT\ln K}$$

Vant Hoff's eqn.

And that is connected to the Gibbs free energy(ΔG) by this equation -RT ln K which is can be found from the Vant Hoff's situation. So, once we know a particular systems acid base equilibria's pKa value we can have a very good idea of what is actually happening thermodynamically whether it is more favorable or not. And this particular system we can define from the use of the thermodynamics.

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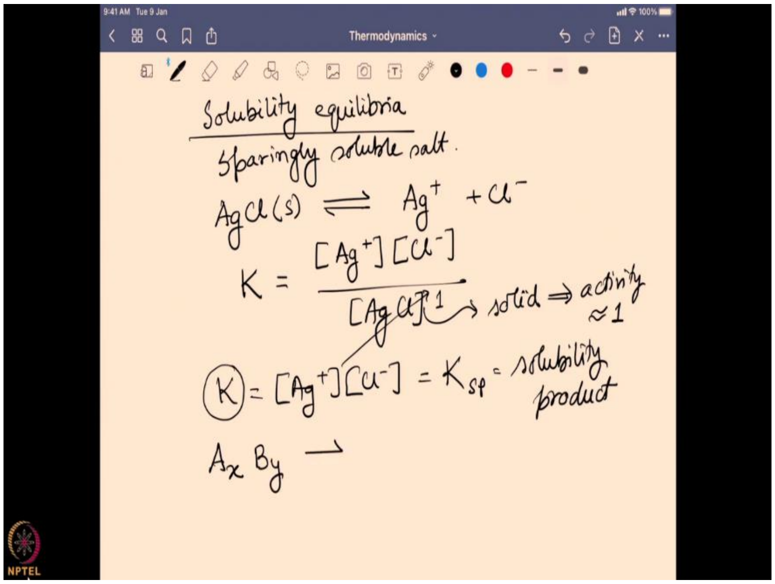

Solubility equilibria

Sparingly soluble salt.

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

$K = \frac{[Ag^+][Cl^-]}{[AgCl]^{1}}$ → solid ⇒ activity ≈ 1

$\boxed{K} = [Ag^+][Cl^-] = K_{sp}$ = solubility product

$A_x B_y \rightarrow$

Now, take a look into a second section solubility equilibria and over there solid equilibria we are talking mostly about a sparingly soluble salt, because for highly soluble salt, it generally goes to the full dissociation of the salt, because that is the most stable state, but in sparingly soluble salt it is not so, it tries to be in equilibrium.

So, we are taking an example of silver chloride, which is in its solid form can dissociates between silver ion and chloride ion. Now, if I want to find the equilibrium constant over here, very similar to our pKa calculation, it will be the product concentrations silver ion and chloride ion divided by the concentration of the silver chloride. $K = \frac{[Ag^+][Cl^-]}{AgCl}$

Now, silver chloride is a solid and that is why we can say its activity is equal to 1. So, we can say it is equal to 1, whereas silver ion and chloride ions are soluble in water, so they are ionic forms. So, this equation remains as $[Ag^+][Cl^-]$ which is nothing but the ionic products of this and this is also known as that K_{sp} or the solubility product.

And the solubility product value gives us an idea about whether the salt is going to be mostly remaining soluble or insoluble. A very high value of K_{sp} means it is mostly going to be soluble and a very low value of K_{sp} which is actually connected with this equilibrium constant value, which shows the equilibrium constant value is pretty low that means this it will be not very soluble in the solution. Now, if I take a general equation of a salt Ax By, and if it is so let me take that to the next page.

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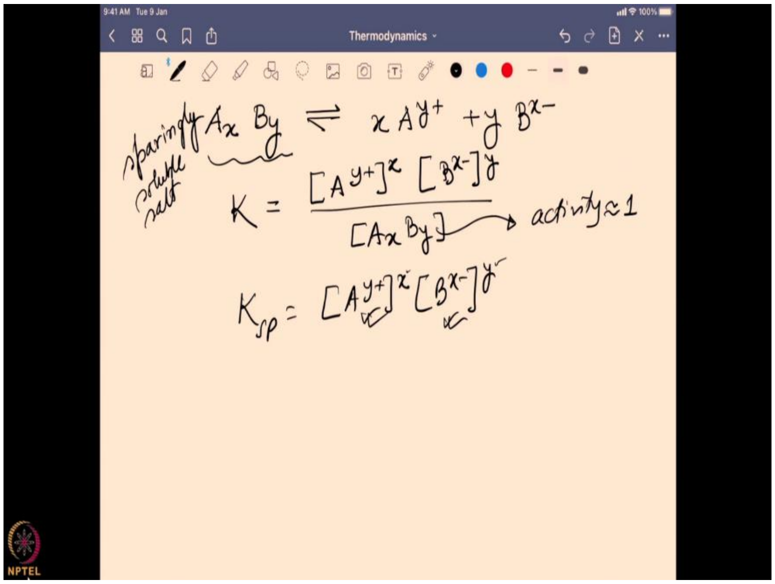

sparingly soluble salt

$$\underbrace{A_x B_y} \rightleftharpoons x A^{y+} + y B^{x-}$$

$$K = \frac{[A^{y+}]^x [B^{x-}]^y}{[A_x B_y]} \longrightarrow \text{activity} \approx 1$$

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

So, now let us take an equation of a general salt Ax By which actually dissociated in the following way $xA^{y+} + yB^{x-}$, so over here the K_{sp} will be $[A^{y+}]^x$ $[B^{x-}]^y$, so the stoichiometric coefficient will go to their powers and divided by [Ax By]. Now, again Ax By is a sparingly soluble salt we are talking about again it is still a sparingly soluble salt and this Ax By is the activity we can take equal to 1 and so the case K_{sp} value will be $[A^{y+}]^x$ $[B^{x-}]^y$, so which is nothing but if the salt dissociate, how much cation I will get, how much anion I will get find the concentration and multiply with the to the power of their stoichiometric coefficient and that is going to give me the idea about the solubility product of the system.

And we will discuss this in more details when we will solve a problem on the solubility product in the next upcoming section. Now, one of the very nice examples of using of this solubility product as you have just discussed the solubility product can define how soluble a salt could be in aqueous solution if it is a high value or low value from there, we can define how much will be the solubility and we can predict how much anions or how much cations I will be expecting in a solution.

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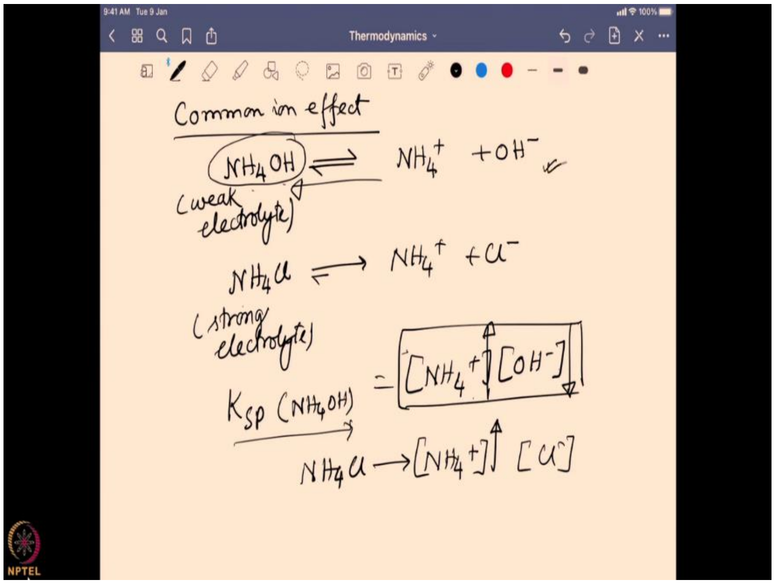

Common ion effect

$\boxed{NH_4OH} \rightleftharpoons NH_4^+ + OH^-$

(weak electrolyte)

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

(strong electrolyte)

$K_{sp}(NH_4OH) = \boxed{[NH_4^+]\uparrow[OH^-]\downarrow}$

$NH_4Cl \longrightarrow [NH_4^+]\uparrow \; [Cl^-]$

Now, there is a very unique effect of this solubility product and that is known as common ion effect. And I am going to explain that with an example. So, I am taking this particular system NH_4OH ammonium hydroxide, it is actually a sparingly soluble system or as we said weak electrolyte that means it does not dissociate completely. So, it gives us some NH_4^+ and some hydroxide ion (OH^-) in the system, and over there can I affect the equilibrium of the system by adding a third party over here.

And that can be done by adding ammonium chloride (NH_4Cl) which is relatively strong electrolyte and that is going to give me a huge amount of $NH_4^+ + Cl^-$. So, now say in a solution, I have a particular amount of ammonium hydroxide present, so according to the solubility product of ammonium hydroxide, I can write it will be the $[NH_4^+][OH^-]$

Now, that is a constant at a particular system, when I added this ammonium chloride what happens? When I added the ammonium chloride in the system, the following thing is happening, it is actually improving the ammonium ion concentration in the solution. So, previously before adding the ammonium chloride, this is actually stabilized with a particular concentration of ammonium and particular concentration of hydroxide, once I started increasing the ammonium concentration that is going to affect the solubility because the K_{sp} value is a constant.

So, they have to keep the solubility product constant that means, if I increase the ammonium ion concentration the hydroxide and concentration should go down, so that their multiplication result the K_{sp} can be a constant, and what will be the after effect of that? The effect will be the hydroxide ion is going down that means it is going to bind some of the ammonium and going back towards this equilibrium.

So, that means most of the ammonium ion which is actually available after we put the ammonium hydroxide in the presence of ammonium chloride some of the ammonium hydroxide will come back to its original insoluble part, because excess ammonium coming from the ammonium chloride is actually driving this equilibrium towards the left hand side.

So, that is known as common ion effect and by that we can tune the reactivity of a particular salt if I want lower amount of concentration of a salt or I want to fine tune that I can always use this common ion effort to control this system. So, this is another nice example of the solubility equilibria and again the K_{sp} value is connected with the equilibrium constant of this weak electrolytes dissociation which can be directly connected to the thermodynamic product, property the Gibbs free energy in the form of $\Delta G = - RT \ln K$. So, over here will conclude this particular section of the application of the thermodynamics. Thank you.